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THE CHEMICAL COMPOSITION OF LIME-SULPHUR ANIMAL DIPS.

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The literature on the subject of lime-sulphur solutions is already voluminous. But even the ablest investigators have been handicapped by limitations in their methods of analysis, while some of the published work, especially in recent years, has been of such a character as to bring the whole matter into a state of confusion. Inasmuch as the writer has been able to develop some new methods of analysis[1,2a] which appear in several ways superior to former ones, it has been a logical step to utilize these new methods in a general study of the composition of lime-sulphur solutions. The information so obtained appears to determine decisively some facts which previously could be only a matter of conjecture or at least only qualitatively studied, and others which have been the subject of dispute, although it very likely brings out little radically new. Lime-sulphur solutions are of considerable practical importance and precise information regarding them is of distinct value.

EXPERIMENTAL MATERIALS AND METHODS.

The general plan of investigation was necessarily simple, merely involving the preparation of solutions according to different formulas and under different conditions, with subsequent analyses and com-

[a] The figures refer to the list of references at end of bulletin.

parison of results. The lime used was prepared from chemically pure calcium oxid by slaking and drying out, then passing through an 80-mesh sieve. Its content in available calcium oxid was determined by the phenol solution method of Lindet and Brasart.[3] The sulphur used was sifted U. S. P. flowers, assumed without analysis to be sufficiently pure for the purpose.

The methods of analysis have been fully described in the previous papers referred to. For the sulphid-acid figure "Method B" was employed, while the sulphid-base figure was not directly determined, since it can be obtained with greater accuracy by algebraic addition of the sulphid-acid figure and the reaction figure. All determinations were performed in duplicate.

EFFECT OF STORAGE.

EXPERIMENT 1.

The first series of experiments, as it happened, was directed toward a study of the stability of lime-sulphur solutions during storage. A number of preparations made for another purpose had been partially analyzed when other matters interrupted. On resumption of the work it seemed best to repeat all the determinations previously executed. The results are given in Table 1, under Experiment 1.

The formulas employed were based on 100 parts of sulphur in all cases, while the lime is expressed in proportional parts available calcium oxid. The proportional parts of water given include both water added as such and the water of hydration of the lime. The lime and sulphur were thoroughly mixed dry in the container in which the solution was to be prepared—a 500 c. c. Kjeldahl flask. The desired amount of water, usually 200 c. c., was then added gradually with thorough mixing. The mixtures were brought to boiling under reflux in about five minutes, and only the period of actual boiling was counted. Shortly before the end of the boiling period, during which the flask was frequently shaken, a stream of illuminating gas washed through caustic-soda solution was introduced through a narrow tube passing down the condenser into the neck of the flask. The flask was partially cooled under these conditions by immersion in water, then the well-mixed contents were transferred to 4-ounce "sample oil" bottles, which were filled into the necks and sealed. When cold the bottles were thoroughly shaken to insure a uniform solution.

The results of Experiment 1 show that within the range of practice, no matter what the formula or conditions of preparation may have been, all lime-sulphur solutions stored after decantation from sediment will acquire a distinct negative reaction figure in course of time. Divers and Shimidzu[4] qualitatively showed the reversibility of the reaction, simply stated: $CaS_x + 2H_2O \rightleftarrows Ca(OH)_2 + H_2S + (x-1)S$. In Experiment 1 we evidently have quantitative data relative thereto. The course of the equation from left to right is a matter of hydrolysis and the reaction evidently will progress thus in all solutions until inhibited by the accumulation of hydrogen sulphid, provided the latter is not allowed to escape. The more dilute

the solution naturally the greater will be the degree of hydrolysis before equilibrium is reached. The free calcium hydroxid simultaneously produced reacts with the free sulphur or with polysulphur, and is thus removed from the sphere of action, the whole series of reactions therefore becoming irreversible.

According to the above hypothesis there should be a slight decrease of polysulphur and a slight increase of both monosulphur and thiosulphate sulphur during storage. This is not consistently true of the concentrates of Experiment 1. On the contrary concentrates A to E, inclusive, suffer a distinct though slight decrease in thiosulphate figure. But the diluted solutions of samples C and E do give more positive indications of the correctness of the above view, though such slight differences can hardly be considered as of much significance in either direction. In this connection it seemed well to try the effect of the addition of calcium hydroxid to a dilute lime-sulphur solution.

TABLE 1.—*Effect of storage upon analytical figures; concentrates diluted to 8 volumes.*

Experiment No.	Sample No.	Formula: CaO:S:H_2O.	Time boiled.	Storage over sediment.	Storage decanted.	Storage diluted.	Reaction figure.	Thiosulphate figure.	Sulphid-acid figure.	Polysulphur figure.
			Hours.	*Days.*	*Days.*	*Days.*				
1	A–1	40:100:513	1	3	0	0	−0.30	6.03	21.08	.....
	A–2			71	0	0	−0.30	5.90	21.28	40.62
	B–1	45:100:514	1	1	0	0	−0.35	6.52	23.69	.....
	B–2			1	63	0	−0.37	6.36	23.71	45.47
	C–1	47.5:100:515	1	1	0	0	−0.66	6.92	25.10	.....
	C–2			1	61	0	−0.17	6.87	24.65	44.37
	C–3			1	0	74	−0.97	6.88	25.25	43.83
	D–1	50:100:516	1	1	0	0	+0.03	7.06	25.95	.....
	D–2			1	61	0	−0.13	6.91	25.94	43.61
	E–1	60:100:519	1	4	0	0	+0.06	7.14	24.81	.....
	E–2			4	62	0	−0.14	6.94	25.06	41.83
	E–3			4	0	94	−0.73	7.10	25.46	40.89
	F–1	45:100:514	0.5	2	0	0	−0.29	6.32	23.72	.....
	F–2			2	62	0	−0.15	6.42	23.49	45.78
	G–1	45:100:514	0.25	1	0	0	+0.26	5.74	21.42	.....
	G–2			1	33	0	0.00	5.87	21.27	40.52
2	G–3	Special.	.....	.....	.....	.....	+3.34	6.11	22.84	39.45
11	R–1	Special.	.....	.....	.....	.....	−0.43	6.17	28.56	49.09
	R–2	Special.	.....	.....	.....	.....	−0.01	12.41	15.52	30.92

EFFECT OF LIME ADDED AFTER DILUTION.

EXPERIMENT 2.

To about 110 c. c. of sample G–2, which had been stored 27 days after dilution, was added slaked lime equivalent to about 2 grams calcium oxid, and the mixture was kept at room temperature in a filled and sealed bottle for 10 days. Each working day, except the last two, when it was left to settle, the bottle was placed in a shaking machine for several hours. The results of analysis are given in Table 1, under Experiment 2, sample G–3.

The changes in the analytical figures between samples G–2 and G–3 are entirely consistent. But it is interesting to note the extreme slowness with which calcium hydroxid reacts with calcium penta-

sulphid in cold dilute solution. Despite the intimate contact of the materials for 10 days and the high plus reaction figure at the end, the analytical figures for the various forms of sulphur were only slightly affected, and the value of x in CaS_x was reduced from 4.81 in sample G–2 only to 4.45 in sample G–3. Therefore for horticultural spraying purposes it appears that lime may be added to the diluted solutions shortly before use without seriously affecting the various sulphur compounds.

After completion of the preliminary experiments on the effect of storage, the main investigation could be undertaken on the effect produced by varying formulas and conditions.

EFFECT OF VARYING LIME-SULPHUR RATIO.

EXPERIMENT 3.

Here lime was the only variable, the amount of sulphur and water and the period of boiling being maintained constant. The concentrated solutions were prepared as described under experiment 1, and, in fact, the majority of them were the same samples, as shown by the identification letters. All determinations were made on freshly prepared dilutions of concentrates which had been stored not less than two months after decantation from sediment, except in case of sample G, stored for 33 days. The results are given in Table 2.

With increasing proportion of lime the percentage of thiosulphate sulphur increases throughout, but the parallelly increasing percentage of monosulphur, together with other analytical values, drops after passing Preparation D merely on account of deposition of polysulphid in crystalline form, as is well known to occur sometimes in preparations made with an excess of lime. Polysulphur reached its maximum value at the lime-sulphur ratio 0.45 in Preparation B, as did also total sulphid sulphur, although total sulphur continued to make a very slight further gain. But probably the most illuminating results are shown by the analytical ratio of total lime to total sulphur. Equal utilization of lime and sulphur begins with Preparation B, where the analytical ratio 0.450 comes out exactly the same as the formula ratio. An excess of sulphur over that ratio, as in Preparation A, produced no higher polysulphid and simply was not utilized. With increasing lime-sulphur ratio equal utilization of lime and sulphur continues certainly into the close vicinity of the ratio 0.500, though at that point results begin to be obscured by the deposition of crystals. But increased ratio means a lower polysulphid, as is clearly shown.

For each molecule of thiosulphate formed in the reaction there was produced an average of about 1.84 molecules of polysulphid. The individual variations from the average seem in no way to be consistently dependent upon variations in formula. This ratio will be discussed later.

TABLE 2.—*Composition in grams per 100 c. c. ("per cent") and ratios of stored concentrates prepared under varying formulas and conditions.*

Experiment No.	Preparation No.	Formula: CaO:S:H_2O.	Time boiled.	Thiosulphate sulphur.	H_2S sulphur.	Total monosulphur.	Polysulphur.	Total sulphid sulphur.	Total sulphur.	Total equivalent CaO.[a]	Analytical ratio. Total CaO / Total S.	Value of x in M_2S_x.	Molecular ratio, $\frac{M_2S_x}{M_2S_2O_3}$.
			Hours.										
	A	40:100:513	1	3.02	0.04	2.73	10.43	13.16	16.18	7.35	0.454	4.82	1.81
	B	45:100:514	1	3.26	.05	3.04	11.67	14.71	17.97	8.09	.450	4.84	1.86
3	C	47.5:100:515	1	3.52	.02	3.16	11.39	14.55	18.07	8.57	.474	4.60	1.80
	D	50:100:516	1	3.54	.02	3.33	11.20	14.53	18.07	8.89	.492	4.36	1.88
	E	60:100:519	1	3.56	.02	3.22	10.73	13.95	17.51	8.70	.508	4.33	1.80
	F	45:100:514	.5	3.29	.02	3.01	11.75	14.76	18.05	8.12	.450	4.90	1.83
4	G	45:100:514	.25	3.01	.00	2.73	10.40	13.13	16.14	7.41	.459	4.81	1.81
5	H	45:100:1014	.75	1.77	.05	1.61	6.10	7.71	9.48	4.37	.461	4.79	1.82
	I	45:100:264	.5+	2.38	.03	5.63	21.20	26.83	29.21	11.94	.409	4.77	4.74

[a] Estimated by calculation from the results for the various forms of sulphur—not by direct determination.

The figures for hydrogen sulphid sulphur in themselves possess little significance from a quantitative point of view, the exact amount present depending upon variable factors. But the figures can be utilized to obtain a nearer approximation to the value of x in CaS_x than given in the table for the value in M_2S_x. If this form of sulphur is present only as free hydrogen sulphid, then the value for x in CaS_x of Preparation B becomes 4.92, while if all hydrogen sulphid is present as calcium hydrosulphid the value of x is raised to exactly 5.00. All the other preparations under Experiment 1 naturally give lower values.

The next undertaking was to determine the effect of varying the period of boiling.

EFFECT OF VARYING PERIOD OF BOILING.

EXPERIMENT 4.

Using the formula 45 : 100 : 514, which had shown the best utilization of both lime and sulphur in Experiment 3, concentrates were prepared, diluted, and analyzed exactly as described under Experiment 3, except in the period of boiling. The results are given in Table 2. With Preparations F and G is also to be included Preparation B, under Experiment 3, as the first member of the series.

Under the conditions of Experiment 4, boiling for 0.5 hour and for one hour produced practically identical results; that is, boiling for the shorter period appeared to produce as complete and perfect a reaction as possible, while boiling for a further half hour seemed to effect no material injury. The higher value for x in M_2S_x shown after 0.5 hour boiling is chiefly due to the less amount of hydrogen sulphid which happened to be present. Assuming free H_2S the value of x in CaS_x is 4.94, and assuming $Ca(SH)_2$ it is 4.98.

On the other hand, boiling for 0.25 hour was plainly insufficient. All percentages are lower and so is the value of x in M_2S_x, while the original reaction figure before storage was positive (Table 1).

Next came a study of the effect of varying the concentration at which the boiling was conducted.

EFFECT OF VARYING CONCENTRATION.

EXPERIMENT 5.

The concentrates were prepared as described for the previous experiments, and the results are given in Table 2. Preparation H was boiled only 0.75 hour since the odor of hydrogen sulphid had then become very strong and Experiment 4 had shown no essential difference between boiling for 0.5 and one hour. In case of Preparation I the ingredients made such a thick mixture that the flask was first heated for 0.75 hour in a boiling-water bath with frequent shaking and constant passage of alkali-washed illuminating gas, then the preparation was finished by boiling for 0.5 hour in the usual way. Preparation B, Experiment 3, is also to be included in this group, being the middle member of the series.

The more dilute preparation, Preparation H, showed results entirely comparable with Preparation B (Experiment 3). The apparently lower value for x in M_2S_x is due to the relatively larger amount of hydrogen sulphid. Assuming free H_2S, the value of x in CaS_x is 4.94; assuming $Ca(SH)_2$ it becomes 5.09.

In case of the more concentrated preparation, Preparation I, there is evident a striking rise in the molecular ratio of polysulphid to thiosulphate. This well-known phenomenon in the preparation of highly concentrated solutions has been ascribed by Van Slyke et al.[5] to the decomposition of calcium thiosulphate into calcium sulphite and sulphur. Notwithstanding the additional amount of sulphur thus rendered available the value of x in M_2S_x suffers a distinct drop in comparison with Preparations B and H, rendered more noticeable if calculations are made to actual CaS_x. Parallelly, Küster and Heberlein[6] found the value of x in Na_2S_x to be highest at a certain optimum concentration, decreasing when the solution was made either more concentrated or more dilute.

A question which here naturally arises is whether there is any more complete utilization of the raw materials at one concentration than at another. This can be answered approximately by comparing the weights of monosulphur in Preparations H, B, and I. Letting W stand for the weight of monosulphur, and v for the volume of dissolved substance, the three following equations hold:

(1) for Preparation H; $W=.0161\ (v+1014)$
(2) for Preparation B; $W=.0304\ (v+\ 514)$
(3) for Preparation I; $W=.0563\ (v+\ 264)$

In these three equations v may be taken as practically a constant quantity. Therefore eliminating v in equations 1 and 2 and solving for W we have W=17.1. In the same way from equations 1 and 3 we have W=16.9, and from equations 2 and 3, W=16.6. Accordingly the utilization of the raw materials appears to become slightly less complete with increasing concentration.

OCCURRENCE AND RELATIONS OF CALCIUM SULPHITE.

While Van Slyke and his coworkers undoubtedly established the presence of calcium sulphite as a frequent ingredient in the sediment from lime-sulphur solutions certain points seemed to call for additional investigation. Particularly was it desired to ascertain if lessened solubility of calcium thiosulphate in liquids heavily loaded with other calcium salts might deserve consideration.

EXPERIMENT 6.

First, 50 c. c. of Preparation I was boiled for five minutes under gas and reflux with 5 grams of calcium sulphite. After several days standing a 15-volume dilution gave a thiosulphate figure of 2.01 against a figure of 2.47 for a similar dilution of the original material. The other analytical figures showed no change except very slight increases attributable to loss of water.

Second, a portion of Preparation H was treated in the same way. A 5-volume dilution prepared the following day gave a thiosulphate figure of 6.98 against a figure of 5.53 for a similar dilution of the original material. Boiling in the same way for 15 minutes longer raised the figure to 8.54.

Third, about 100 c. c. of Preparation I with 10 grams calcium thiosulphate in a filled and sealed bottle was mechanically shaken several hours at room temperature. A 15-volume dilution of the supernatant liquid had a thiosulphate figure of 5.42 against the figure of 2.47 for a similar dilution of the original material. A clear decanted portion of the concentrate thus treated was then heated in a flask provided with a vertical air condenser for one hour in a boiling-water bath. Much sediment appeared. After settling for several days a 15-volume dilution had a thiosulphate figure of 2.91. The other analytical figures showed no significant differences from the corresponding figures of the original untreated Preparation I. The insoluble residue produced was washed with cold distilled water until free from the yellow color of polysulphids. A portion suspended in water showed a slightly alkaline reaction with phenolphthalein, and absorbed a large quantity of strong iodin solution. During addition of iodin solution the odor of sulphur dioxid became at one stage very distinct. After excess of iodin had been added and then removed by sodium thiosulphate the resulting liquid was strongly acid to methyl orange, all of which reactions combined constitute conclusive proof of the presence of sulphites.[7]

By Experiment 6 the equilibrium of the reaction $CaS_2O_3 \rightleftarrows CaSO_3 + S$ is controlled by both temperature and concentration of the solution. Highly concentrated solutions can dissolve in the cold much more calcium thiosulphate than naturally occurs in them, but on heating the above reaction progresses from left to right. On the other hand,

calcium sulphite added to boiling dilute solutions reacts with polysulphur and forms thiosulphate. Therefore in practice there must be a fairly definitely fixed concentration below which sulphite will not be permanently formed in significant amount during the preparation of lime-sulphur solutions, lying somewhere between 3.04 and 5.63 per cent of monosulphur. It seemed desirable to fix this critical concentration a little more closely.

EXPERIMENT 7.

Preparations of intermediate concentration were prepared in the usual manner except that a decided excess of lime was used and boiling continued for 1.25 hours or longer. Preparation K was found to contain 3.33 per cent monosulphur with a ratio $M_2S_x : M_2S_2O_3 = 1.82$. Preparation L contained 3.95 per cent monosulphur with a ratio $M_2S_x : M_2S_2O_3 = 3.79$.

By this experiment, in addition to which further tests did not seem worth while, the critical concentration lies between 3.33 and 3.95 per cent monosulphur, which, assuming that one-sixth of the sulphur is converted to monosulphur, corresponds in the formula to the use of respectively 20 and 23.7 grams of sulphur per 100 c. c. of finished solution.

RATIO OF POLYSULPHID TO THIOSULPHATE.

For many years it has been unquestioned that the primary reaction between lime and sulphur in water is: $3Ca(OH)_2+(2x+2)S=2CaS_x+CaS_2O_3+3H_2O$, which equation of course calls for a ratio of 2 between the molecules of polysulphid and thiosulphate produced. The ratios actually obtained in Experiment 2, as already noted, all fell considerably below the theoretical figure. Part of the discrepancy may be ascribed to hydrolysis with subsequent loss by volatilization of the hydrogen sulphid, and part to oxidation, since the conditions of the experiments were only such as to minimize, not absolutely exclude, contact with air. It seemed desirable to ascertain how nearly the theoretical ratio could be reached under more favorable conditions.

EXPERIMENT 8.

A fifth of the formula 45:100:1014 was charged into a stout bottle, the small remaining space being filled with washed illuminating gas, and the tightly stoppered bottled was attached to a shaking machine and immersed in a water bath. After heating for 0.5 hour the originally cold bath had reached a temperature of 80° C. and the liquid in the flask had become decidedly yellow. Further heating rapidly deepened the color until after 0.75 hour from the start a temperature of 95° C. was reached, after which the bath was maintained at 90° to 95° C. for one hour longer. The bottle was then removed from the bath and cooled in running water. When it was opened the odors of illuminating gas and of hydrogen sulphid were strong. A 4-volume dilution was made the next day and analysis gave the molecular ratio M_2S_x; $M_2S_2O_3 = 1.89$. (Preparation M.)

To eliminate the disturbing effect of hydrolysis which had evidently occurred, Preparation N was made by charging 20 grams sulphur and slaked lime equivalent to 9 grams available calcium oxid into a 4-ounce sample oil bottle, which was then filled with water and sealed. For some weeks the bottle was shaken by machine several hours each working day, but the action was so slow that finally it was simply given a brief shaking by hand once or twice a day. After 42 days a sample of the clear liquid, diluted to 2 volumes, showed the molecular ratio $M_2S_x : M_2S_2O_3 = 1.92$.

The last preparation suffered a slight exposure to air while the necessary degree of dilution for analysis was being ascertained. To get further light on the possibilities Preparation O was similarly made, but using only 10 grams sulphur and employing a slight calculated excess of caustic soda solution instead of lime. In 5 days the sulphur was entirely dissolved, and on the next day a 4-volume dilution showed the molecular ratio $M_2S_x : M_2S_2O_3 = 1.93$. The dilution had been prepared by pipetting 25 c. c. into a 100 c. c. volumetric flask about half full of water, then making to the mark. The diluted solution was filled into 15 c. c. glass-stoppered bottles, one of which was used for each test. Freshly boiled water was used for the original preparation and for the dilution.

From Experiment 8 it is evident that the fundamental reaction between lime and sulphur is parallel to that between caustic soda and sulphur and it must be assumed that two molecules of polysulphid are produced for each molecule of thiosulphate. The analytical methods are not known to be at fault except in a minute error of end-point, arising from the necessity of obtaining the sulphid-acid figure by subtraction. The chief cause of the failure to reach the theoretical ratio must, therefore, be oxidation during the manipulation of the solutions. An oxidation of 1 per cent of the monosulphur to thiosulphate by calculation would produce a drop in the ratio from 2.00 to 1.94.

LOWER POLYSULPHIDS; EFFECT OF EXCESS OF LIME.

The composition of the crystalline polysulphid which sometimes forms in a solution prepared with excessive lime has received considerable previous study with conflicting results.[8] It seems, however, to have been proved to be a basic polysulphid which is decomposed when treated with water into calcium hydrate and a soluble calcium polysulphid that was first stated by Schöne to be tetrasulphid. For present study the composition of the crystals themselves is immaterial, since we are only concerned with polysulphids in solution. So far as work subsequent to Schöne has covered the question it has only served to confirm his observations and to strengthen the hypothesis that tetrasulphid is the lowest polysulphid ever occurring in a lime-sulphur solution. Only the following experiment was, therefore, thought necessary.

EXPERIMENT 9.

Preparation P, originally intended to follow Preparation E in Experiment 3, was made on the formula 70 : 100 : 521, boiling for one hour. After standing

over sediment for 74 days, during which time a considerable quantity of crystals formed, the supernatant liquid was decanted and analyzed. The bottle was then filled with water, the sediment broken up, and the corked bottle mechanically shaken for several hours. The supernatant liquid was in turn decanted, and the sediment, which still contained orange crystals, was once more extracted in the same way. The values of x in M_2S_x were found as follows: Original solution, 4.33; first extract, 4.17; second extract, 4.04. Using the thiosulphate figures as an index of the amount of mother liquor remaining in each extract gave x=3.75 for the CaS_x of the original crystals and x=3.97 for the crystals remaining after the first extraction, though these figures must of course be regarded as only approximations.

Experiments 1 and 3 had seemed to show that the use of an excess of lime necessarily produced in the fresh preparations a distinctly plus reaction figure and a considerable proportion of tetrasulphid. But the preparations there made had been rather intimately mixed with their sediments during and after cooling under conditions not entirely comparable to the ordinary. Accordingly, further experiments were undertaken.

EXPERIMENT 10.

Preparation K, already mentioned under Experiment 7, made with excessive lime, after boiling for 1.5 hours, was allowed to cool slightly under gas, mixed, allowed to settle a moment, and then decanted from most of the sediment into a 200 c.c. stout flask which was filled almost full and stoppered. The flask was immersed in a water bath set on the steam bath and left at rest for about 0.75 hour at 70° to 75° C. The still slightly cloudy solution was decanted through cotton, through which it filtered perfectly clear. After about two hours, when the solution had become thoroughly cold, an 8-volume dilution showed a reaction figure of —0.02 and a value of x in M_2S_x=4.40.

Sample Q was prepared in the regular apparatus with excess lime, but boiled for only 0.25 hour. After cooling five minutes under gas with frequent shaking sediment and all were brought onto a cotton filter, except for a portion of mixed sediment and liquid separately preserved. In about three hours crystals had formed in the sediment of the unfiltered material, but none appeared then or after several days in the filtered solution. A portion of the latter, about three hours after preparation, was diluted to eight volumes, and the diluted solution showed a reaction figure of +0.47 with a value of x in M_2S_x of 4.77. The concentrate contained 2.95 per cent monosulphur.

As respects reaction figures, it is evident that a preparation carrying excess of lime, if cooled in intimate contact with its sediment, will very naturally possess a plus reaction figure. But if the preparation is allowed to settle in the heat, undissolved calcium hydrate is rapidly deposited and so removed from further activity, while the small amount remaining in solution soon disappears through reaction with pentasulphid. Hydrolysis will finally produce a minus reaction figure. The latter conditions of course more nearly parallel those prevailing in practice.

The marked difference in the values for x in CaS_x shown by Preparations P and Q is also of interest. It seems futile to speculate on what particular polysulphid may be the immediate product of

the reaction between lime and sulphur. To the writer it appears logical to believe that in a boiling solution containing both lime and sulphur, that is, an unfinished solution like Preparation Q, there is little but pentasulphid present. If any lower polysulphid really is the first product, it apparently at once takes up more sulphur and becomes pentasulphid. Especially is this likely to be true from the well-known fact that hot solutions can dissolve notably more sulphur than corresponds to the formula CaS_5. If the foregoing is granted, then it follows that tetrasulphid present at the end has mainly resulted from the secondary reaction of pentasulphid with lime.

HIGHER POLYSULPHIDS; EFFECT OF OXIDATION.

When a lime-sulphur solution is exposed to air, calcium polysulphid is oxidized to calcium thiosulphate and sulphur. It seems rational that in the presence of this nascent sulphur calcium polysulphid remaining undecomposed should pass to the highest possible stage of sulphurization, and that data thus obtained regarding the highest polysulphid of calcium existing in solution should be much more trustworthy than those derived from the rather dubious method of Auld [8] which led him to infer the existence of polysulphids much higher than the pentasulphid.

EXPERIMENT 11.

A portion of a dilution prepared about two months previously from a concentrate of high lime-sulphur ratio was vigorously shaken in a flask connected without exit tube with a small gasometer of pure oxygen. A considerable quantity of oxygen was absorbed while the solution remained perfectly clear, during which stage the nascent sulphur was evidently wholly entering combination to produce higher calcium polysulphids than were originally present. At a certain point, however, the solution suddenly became opalescent, and thereafter rapidly increased in turbidity. Treatment with oxygen, which altogether occupied but a brief time, was stopped when a considerable quantity of free sulphur appeared present, and the solution was transferred to a well-filled and sealed bottle. Vigorous shaking coagulated the sulphur, but some air had become entangled, so it was necessary the next day to filter rapidly through a loose plug of cotton, after which both the original solution (sample R–1) and the oxidized solution (sample R–2) were analyzed. The titration results are given in Table 1.

The value of x in the M_2S_x of sample R–1 was, therefore, 4.44, while after oxidation the value of x in CaS_x for sample R–2 rose to 4.99. Another experiment in which a very slow current of air was bubbled for a long time gave exactly the same figure. Therefore it is plain that a lime-sulphur solution as applied in practice never contains a calcium polysulphid higher than the pentasulphid. On the other hand any lower polysulphid present in the solution before application probably becomes pentasulphid through free contact with air soon after if not during the process of application.

It is interesting to note the change in reaction figure between samples R–1 and R–2. The change is, of course, perfectly logical, for the hydrogen sulphid which produces the negative reaction figure becomes simply sulphur and water upon oxidation. In deducing the equation to express oxidation, it is accordingly necessary in this case to employ the sulphid-base figures and not the sulphid-acid figures. The change of sulphid-base figure from sample R–1 to sample R–2 is 28.13–15.51=12.62 loss, which, according to the accepted equation $CaS_x+3O=CaS_2O_3+(x-2)S$, should be balanced by a gain of one-half as much, or 6.31, in the thiosulphate figure. The actual gain in the thiosulphate figure in the experiment was 6.24, which is in reasonable agreement.

CONCLUSIONS.

The reactions which determine the composition of lime-sulphur solutions, besides being rather numerous, are some of them reversible, the points of equilibrium varying according as the solution is hot or cold, dilute or concentrated, or exposed to the influence of other varying conditions. Under such circumstances the only way in which laboratory studies can be of practical value is by so thoroughly establishing the fundamental principles involved and the effect of varying conditions upon the relative importance of such principles as to afford a sound basis for reasoning.

It appears that when lime and sulphur are boiled with water, ignoring unessential and hypothetical intermediate compounds, the following reactions occur:

(1) $3Ca(OH)_2+12S=2CaS_5+CaS_2O_3+3H_2O$

(2) $10CaS_5+3Ca(OH)_2=12CaS_4+CaS_2O_3+3H_2O$

(3) $CaS_4+S=CaS_5$

Only when substantially all free sulphur has been dissolved will equation 2 become operative or equation 3 fail to hold all polysulphid substantially up to the pentasulphid.

All lime-sulphur solutions are subject to hydrolytic decomposition according to the equation:

(4) $$CaS_x+H_2O\rightleftarrows Ca(OH)_2+H_2S+(x-1)S,$$

the pressure of the reaction from left to right increasing with rise of temperature. Whether or not hydrogen sulphid can escape, the remaining products on the right-hand side react according to equation 1, giving as final result, in case of CaS_5,

(5) $$CaS_5+3H_2O=CaS_2O_3+3H_2S.$$

Thus all solutions are in equilibrium only when they contain a certain excess of hydrogen sulphid, the amount being dependent upon the temperatures and concentrations of the solutions.

Solutions exposed to air are oxidized, as is usually represented by the equation:

(6) $$CaS_x+(x-2)O=CaS_2O_3+(x-2)S,$$

although it is possible that, as propounded by Divers and Shimidzu, the immediate action is an oxidation of the hydrogen sulphid liberated according to equation 4.

Above a certain concentration of the hot solution, which appears to lie between 3.33 and 3.95 per cent of monosulphur, the following reaction tends to progress from left to right:

(7) $$CaS_2O_3\rightleftarrows CaSO_3+S.$$

A well-boiled solution, not originally made with an excess of lime, can never under any circumstances possess a plus reaction figure—that is, it can not contain calcium hydroxid in excess of monosulphur. If originally made with an excess of lime or if not boiled long enough, excess lime is at first present in solution. But if such a preparation be allowed to stand quietly and cool off in the cooking vat, the indications are that the undissolved lime soon settles down, while the small amount of dissolved lime rapidly reacts with polysulphur according to equation 2, so that in this case, also, unless the cooled solution is again stirred up with the sediment, a plus reaction figure can never be present in the end. But such a solution will naturally contain a notable amount of tetrasulphid.

As regards the period of boiling, it is not improbable that the time should be increased with increasing concentration. Lime is but little soluble in the solution at any stage, and it probably must dissolve before it can react with the sulphur. It would seem, therefore, that a longer time must necessarily be required in a given volume for a large quantity of lime to enter successively into solution and into reaction than for a small quantity.

As regards the effect of degree of concentration, in addition to the decomposition of thiosulphate which has been noted, the indications are that with increasing concentration the utilization of both lime and sulphur possibly becomes less nearly complete, and also that the polysulphids formed possibly contain a somewhat less proportion of pentasulphid. But the apparent effect might have been produced simply by insufficient boiling, and in any event it is of no material significance in comparison with the practical importance of putting out proprietary preparations in highly concentrated form.

Finished solutions, if stored over sediment which contains free lime, will naturally tend to maintain a plus reaction figure and will undergo changes attributable to the slow progress of reactions 1 and 2. If decanted from sediment and preserved from access of air, only two slight changes are noticeable; first, the progress of equation 5 until a certain concentration of hydrogen sulphid is reached, when equilibrium is established according to equation 4;

second, an apparent slight drop in the thiosulphate figure, for which no explanation is offered, since the phenomenon appeared too quantitatively insignificant to warrant special investigation. Both changes, in fact, are so slight as to be entirely negligible for practical purposes and under ordinary conditions.

For the actual preparation of lime-sulphur solutions equations 1, 2, and 3 call for the use of 43.7 parts of available calcium oxid to 100 parts sulphur. That the laboratory experiments did not precisely check this theoretical ratio is attributable solely to the decompositions represented by equations 5 and 6. The decomposition represented by equation 5 is independent of the formula employed and in no way changes the relative proportions of primary ingredients called for; that is, equation 5, following the postulated escape of hydrogen sulphid, produces neither free lime nor free sulphur, and leaves the solution neutral. There remains then only the matter of oxidation to be considered. But that is a surface action solely, and considering the enormous advantage in the ratio of volume to surface possessed by even moderate-sized cooking vats over laboratory apparatus, it approaches a negligible factor. Therefore the theoretical ratio becomes the actual ratio which should be followed in practice, provided only the concentration is not sufficient to allow equation 7 to progress from left to right. The formation of sulphite becomes a significant factor when the formula employs somewhat more than 20 parts of sulphur per 100 volumes of finished solution. For a number of reasons the writer believes that it will be generally inadvisable to try for a much higher degree of concentration in "homemade" solutions. Certainly in such solutions no allowance should be made for the formation of sulphite by increasing the ratio of lime to sulphur, as the extent of the decomposition is too dependent on the degree of concentration and length of boiling after the solution is otherwise complete. Attempts to make more concentrated solutions are attended by greater difficulty in manipulating the thick liquid and in avoiding loss by boiling over, and moreover involve more loss of the finished solution in the wet sludge, especially since the volume of sludge is increased by deposition of calcium sulphite.

Nowhere is there evidence of the existence in cold solutions of more sulphur, either free or combined, than corresponds to the formula CaS_5. On the other hand, a properly prepared homemade solution will contain at most but a small amount of tetrasulphid. It will also contain a very small amount of hydrogen sulphid, some of which may possibly be in the form of calcium hydrosulphid. While rigidly scientific proof that the two apparently definite proportions of, respectively, four atoms and five atoms of sulphur to one atom of calcium may not, in fact, arise from mixtures of lower and higher

polysulphids is perhaps lacking, it is certainly true that all available evidence points to the existence of only those two.

The methods of analysis have proved to be adequate in scope and accuracy, as well as practical. Working in the ordinary way with flasks and pipettes the analyst apparently will not recover from a concentrate more than 99 per cent of the monosulphur, which indicates a recovery of 99.75 per cent of the polysulphur, or 99.6 per cent of the sulphid sulphur, figuring on pentasulphid only. The loss arises chiefly from oxidation during manipulation of the solutions and may be reduced only by manipulating in an atmosphere of some inert gas.

PRACTICAL APPLICATIONS.

It will be a logical concluding step to deduce from the data here presented a working formula for the preparation of lime-sulphur solutions. The subject has been dealt with by a number of investigators primarily interested in the preparation of such solutions for horticultural spraying purposes. Some of the formulas so developed seem to have given entire satisfaction for the purpose for which they were intended and the dilutions at which the resulting products should be employed under various conditions have become so well established that any change in formula would be of doubtful practical benefit. It is quite otherwise with solutions intended primarily for the purpose of dipping cattle and sheep. The formulas in use are those prescribed by the Bureau of Animal Industry many years ago when uncertainty regarding possible chemical reactions and possible effects of the resulting compounds upon both animals and parasites very properly led to the use of formulas which should be certain and safe, even if somewhat uneconomical. The formula here to be suggested is proposed therefore solely for use as an animal dip. It may be termed the " 8–18–10 " formula; that is, 8 pounds of high grade commercial quicklime, 18 pounds fine sulphur (either flowers or flour) with somewhat more than 10 gallons water, boiled to a volume of 10 gallons at the finish. The time of actual boiling should be one hour. The theoretical ratio between lime and sulphur will be met by this formula if the lime is 98.3 per cent pure, therefore the formula as given is appropriate for preparing a solution for dipping sheep where any chance of an excess of lime must be avoided. If commercial hydrated (not air-slaked) lime is used the amount should be increased nearly one-third, say to 10.5 pounds. For dipping cattle the formula may be used on the basis of available calcium oxid if the analysis of the lime is known, or if not known the lime may safely be raised to 8.5 pounds, corresponding to 92.5 per cent available calcium oxid, possibly even to 9 pounds. The manipulation of the materials in the actual process of preparation has been described in a recent publication from the Bureau.[9]

The finished solution, drawn off from the sediment, should theoretically contain 18 per cent (grams per 100 c. c.) of sulphid sulphur, but probably will contain somewhat less. It is, therefore, appropriate for dipping sheep at a dilution of 1 volume of concentrate to 9 or 10 volumes of water, and for cattle at a dilution of 1 volume of concentrate to 7 or 8 volumes of water. But in any event, since baths lose strength during dipping, it is very desirable to keep them at all times under control by means of a "field test."[10]

The particular advantages of the above formula are, first, that it closely approaches the theoretical ratio, making allowance for impurities; second, it is as concentrated a product as can be prepared without conversion of thiosulphate to sulphite; and third, the figures are easily remembered and readily converted into the quantities of ingredients necessary to prepare a batch of any desired size.

In deducing a formula for the preparation of highly concentrated proprietary solutions it is evident that the manufacturer must make a few trial runs with plenty of sulphur in order to establish the conditions which will uniformly yield the product he desires, analysis of which will then inform him by how much he may safely reduce the sulphur to allow for the formation of sulphite.

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